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14. ABSTRACT

Isolated attosecond pulses are produced with instrumentation developed in a multi-investigator collaborative MURI effort and used for first experiments in attosecond electron dynamics. A new method of ionization phase match gating is developed for isolated attosecond pulse production, and wavelength tunability of the isolated attosecond pulses is achieved. The isolated attosecond pulses are used for optical streak-field spectroscopy experiments conducted in neon and sulfur hexafluoride with both time of flight electron and mass spectrometry, as well as velocity map imaging (VMI) detection. The results reveal the isolated nature of the attosecond pulses, and by high field streaking the pulse contrast is determined. A system is developed to generate high harmonics from low pulse energy pulses by intracavity buildup. An apparatus to perform solid-state experiments using plasmon enhanced surface fields is in operation. Novel soft x-ray optics are produced by the combination of new materials, and the shortest possible pulses (80 as) are achieved by the use of these optics in a European collaboration.

15. SUBJECT TERMS
attosecond, laser, electron dynamics, instrumentation

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The overall goal of the attosecond instrumentation MURI program was to produce isolated attosecond pulses in the soft x-ray (extreme ultraviolet – EUV or XUV) regime and to utilize these pulses for electron dynamics experiments in atoms, molecules, and solids. The program required the marriage of several important techniques: the production of a few cycle driver laser at 800 nm, the carrier envelope phase stabilization of the high pulse energy, few cycle pulse laser, the generation of high order harmonics with control of the harmonic generation process to confine the output to one principal half cycle of the driver pulse, the fabrication of XUV optics, and development of both gas phase and solid state platforms for experiments, the latter solid state system was configured especially for the area of nanoscience with exploratory samples. In the report that follows, several main sections highlight the results along these lines.

I. Frequency combs in VUV/ XUV and Frequency Comb Spectroscopy

Principal Investigator: Jun Ye, JILA, NIST and University of Colorado, Boulder

With revolutionary impact on precision metrology and ultrafast science brought by the recent development of optical frequency combs, the next exciting frontier naturally turned to the production of VUV and XUV frequency combs; laser-like sources with a high degree of temporal coherence in the vacuum and extreme ultraviolet spectral regions. The main motivation for this research direction was the expectation that high precision laser spectroscopy techniques and high resolution quantum control can be utilized in the VUV and XUV, which would allow measurement of many ground state transitions of atoms and molecules with revolutionary precision. By comparing with theoretical calculations, these experiments might allow for some of the most stringent tests ever applied to quantum electrodynamics. The production of VUV and XUV frequency combs also represent important progress towards an ongoing goal; to utilize frequency comb technology to access every frequency range in the electromagnetic spectrum with revolutionary precision. This work will also dramatically enhance the efficiency or coherence of the next generation accelerator-based advanced light sources.

The advance in VUV and XUV frequency comb productions was enabled by the recent demonstrations of high harmonic generation at ~100 MHz repetition frequencies within femtosecond enhancement cavities. To build up a sufficiently high intracavity pulse energy to enable high harmonic generation (HHG), the passive optical cavity needs to demonstrate a number of important characteristics: i) a high finesse, ii) low round-trip group-delay dispersion to allow ultrashort pulses to be coupled into and stored inside the cavity, iii) a robust servo to stabilize the two degrees of freedom of the incident pulse train to the corresponding cavity resonance modes, and iv) a highly efficient output coupling mechanism to introduce the intracavity HHG radiation as a useful beam to the outside world.

When the project was started, a standard modelocked femtosecond Ti:Sapphire laser was used with a repetition frequency of 100 MHz, 60-fs pulse duration, and 8 nJ pulse energy. The pulse train from the laser passed through a prism-based compressor before incident on the passive optical cavity. To investigate the peak intensity that can be obtained with this method, an empty femtosecond enhancement cavity was characterized. With the laser locked to the cavity, the transmitted spectrum showed the effect of the residual cavity

dispersion limiting the intracavity pulse bandwidth. Measurement of the transmitted pulse verified that the pulse was nearly Fourier-transform-limited with a duration of 60 fs. The duration of the pulse was minimized inside the cavity by adjusting the compressor in front of the cavity. The intracavity pulse energy was enhanced up to 4.8 μJ for these short pulses, approximately a 600-fold increase from the incident pulse energy of 8 nJ. Correspondingly, a peak intensity of $>3 \times 10^{13}$ W/cm^2 was obtained at the intracavity focus. Bright Xe plasma was produced at this location. Subsequently, HHG radiation produced in the VUV spectral region was coupled out using an ~700 μm-thick sapphire plate placed at Brewster's angle (for the 800 nm frequency comb) inside the cavity. HHG radiation was detected up to the 9th harmonic of the 800 nm generating pulse.

To improve the efficiency of intracavity HHG and extend the HHG wavelength deep into XUV, the intracavity pulse peak intensity needed to be scaledup. However, a real road block was identified, the intracavity Brewster plate. First, the effect of intracavity nonlinear dynamics was investigated arising from enhanced peak powers of femtosecond pulses inside broad-bandwidth, dispersion-controlled, high-finesse optical cavities. For $\chi^{(3)}$ nonlinearities, when a train of femtosecond pulses were maximally coupled into a cavity by active stabilization of its frequency comb to the corresponding linear resonances of a cavity, enhancement ceased when the peak nonlinear phase shift was sufficient to shift the cavity resonance frequencies by more than a cavity linewidth. In addition, the complex spectral dynamics that resulted from chirping the input pulse was studied and accounted for and excellent qualitative agreement with experimental results obtained. An even more detrimental problem was that the Brewster plate was often damaged when the level of HHG intensity was raised. This had prevented the scaling of this system up to higher powers.

Then novel enhancement cavity configurations were designed without the use of the Brewster plate. The concept was technically very challenging, involving careful engineering of the mirror coatings, custom apertures in the optical substrates, and good servo electronics. In the new cavity geometry, one of the focusing cavity mirrors had a 100-mm hole drilled in the middle. The coupling efficiency and cavity loss associated with such cavity geometry were carefully investigated. By using a higher order cavity mode such as TEM01, build up of sufficiently high peak power inside the cavity for HHG to work was achieved. The generated VUV radiation could leak out of the mirror hole due to the significantly smaller diffraction angle enjoyed by the shorter wavelength beam. This cavity geometry could lead to a larger buildup of the pulse power inside the cavity without the limitation of any intracavity optics. In practice, however, the mode conversion from TEM_{00} to TEM_{01} was lossy and led to a substantial amount of power loss, which was critical for the type of extreme nonlinear optical experiments. The final successful solution was to incorporate an output coupling grating inside the buildup cavity. This concept was realized in the lab and worked extremely well, as shown in Fig. 1.

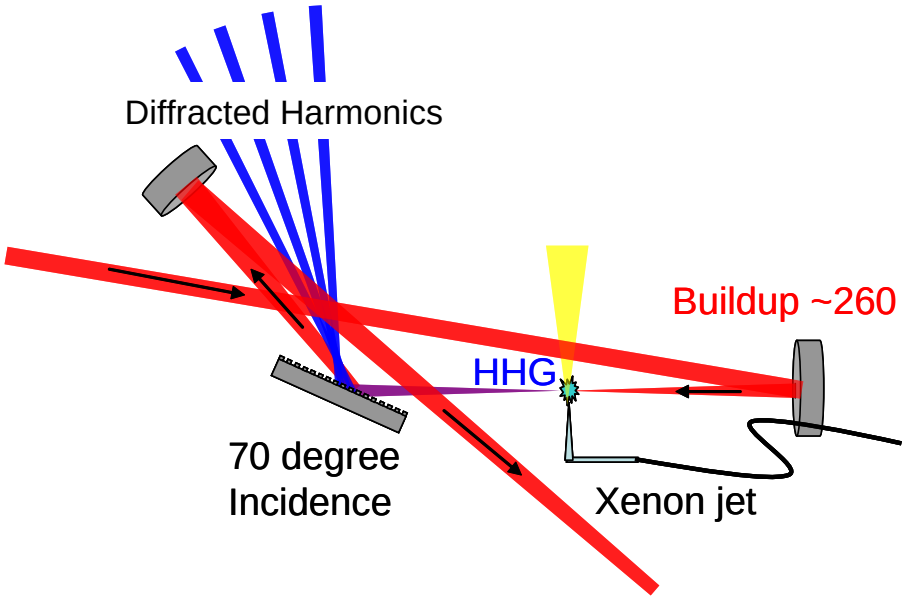

Fig. 1 Femtosecond enhancement cavity for HHG generation to produce XUV frequency combs.

Growing demands for high average and peak powers in extreme nonlinear optics, attosecond pulses, and XUV-comb generation experiments can find a powerful solution in fiber-based mode-locked lasers. Many of the recent advances were enabled by a 10 W Yb:fiber laser based optical frequency comb with record-setting frequency stability. Here it was shown that this frequency comb has a < 1 mHz relative optical linewidth against another conventional frequency combs. This incredible level of frequency stability allowed us to enhance this frequency comb inside an optical enhancement cavity reaching more than 3 kW of average power. With this new source we have been able to produce harmonics up to the 21st (the cutoff in Xe) at 130 MHz repetition rate, with 0.1 - 10 microWatts of average power per harmonic, as shown in Fig. 2. The increase in average power per harmonic allowed the observation of quantum interference between different electron trajectories in the HHG process and, importantly, to demonstrate comb coherence in the HHG radiation for the first time.

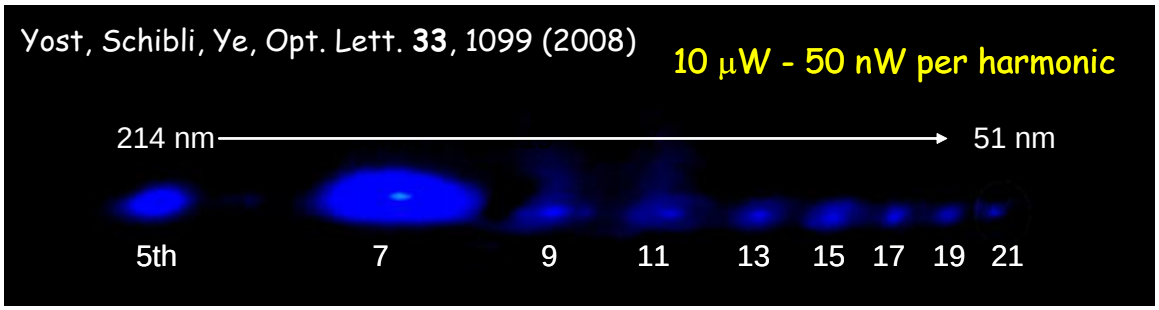

Fig.2 Spectrum of intracavity HHG using Xe.

Thus far, tests of the coherence of VUV combs have only been conducted for the 3rd harmonic. Since high harmonic generation is so nonlinear, it was necessary to demonstrate that a high degree of phase coherence can be maintained throughout this process. To demonstrate the coherence of the higher harmonics, a study of the phase coherence was performed for the 7^{th} harmonic. In order to conduct this coherence measurement, a variation of the delayed self-homodyne method was used. The 7^{th} harmonic radiation was sent through a Sagnac interferometer with the length delay set so that pulse *n* in the pulse train will interfere with pulse *n*+1. There were many technical difficulties in building this interferometer since VUV light is very absorbing and hard to detect but clear interference between subsequent pulses was seen in the pulse train. This measurement effectively an upper bound on the frequency noise and linewidth of the 7^{th} harmonic. This result showed a clear comb structure for the 7^{th} harmonic which really opens the door for the use of VUV frequency combs as a new tool for precision measurement. In other words, for the first time ever, successive VUV pulses separated by more than a few nanoseconds were shown to be phase coherent.

On a related development, cavity-enhanced direct frequency comb spectroscopy was successfully implemented and this technique applied to a number of useful applications. Cavity-enhanced direct frequency comb spectroscopy combines broad spectral bandwidth, high spectral resolution, precise frequency calibration, and ultrahigh detection sensitivity, all in one experimental platform based on an optical frequency comb interacting with a high-finesse optical cavity. Precise control of the optical frequency comb allows highly efficient, coherent coupling of individual comb components with corresponding resonant modes of the high-finesse cavity. The long cavity lifetime dramatically enhances the effective interaction between the light field and intracavity matter, increasing the sensitivity for measurement of optical losses by a factor that is on the order of the cavity finesse. The use of low-dispersion mirrors permits almost the entire spectral bandwidth of the frequency comb to be employed for detection, covering a range of ~10% of the actual optical frequency. The light transmitted from the cavity is spectrally resolved to provide a multitude of detection channels with spectral resolutions ranging from several gigahertz to hundreds of kilohertz. A very good understanding of the principle of cavity-enhanced direct frequency comb spectroscopy has been achieved as well as the various implementations of such systems. In particular, several types of UV, optical, and IR frequency comb sources were discovered and optical cavity designs implemented that can be used for specific spectroscopic applications. Several cavity-comb coupling methods were devised to take advantage of the broad spectral bandwidth and narrow spectral components of a frequency comb. Finally, a series of experimental measurements on trace gas detections, human breath analysis, and characterization of cold molecular beams was demonstrated. These results demonstrate clearly that the wide bandwidth and ultrasensitive nature of the femtosecond enhancement cavity enables powerful real-time detection and identification of many molecular species in a massively parallel fashion.

II. Production of isolated attosecond pulses and gas phase attosecond experiments

Principal Investigators: Stephen Leone and Daniel Neumark, Department of Chemistry, University of California, Berkeley

Over the duration of the MURI grant, the Leone/Neumark group successfully designed and built an apparatus capable of producing isolated attosecond soft x-ray pulses, possibly the first in

North America. This apparatus combined cutting edge technology and theory from several different fields, all of which were required to work in conjunction to achieve the desired results.

The system was started with a commercially purchased amplified laser system (Femtolasers), which produced 25 fs laser pulses at 800 μJ per pulse. One of the first major achievements in the lab was the successful stabilization of the carrier-envelope phase (CEP) of the oscillator laser pulses using homebuilt electronics provided by the group of Jun Ye. The 25 fs laser pulses were then spectrally broadened using a gas filled hollow-core fiber and temporally recompressed to ~6 fs using a chirped mirror compressor. A study was undertaken to find the best spectral broadening scheme for this application, and it resulted in the publication of two papers regarding the hollow-core fiber and filamentation methods. Hollow-core fiber broadening was the method of choice because its spectral profile better matched the reflectivity profiles of the chirped mirrors. After this spectral broadening and temporal recompression to a few optical cycles, the CEP of the amplified laser pulses was stabilized using an f-2f interferometer that fed back into the oscillator pump power.

After generating CEP stabilized few-cycle laser pulses, the Leone/Neumark group used them to generate high-order harmonic radiation in both argon and neon filled gas cells. The soft x-ray harmonic radiation was measured using a home-built x-ray spectrometer. The CEP of the laser pulses was carefully controlled so that one pulse in the emitted train of x-ray pulses would have higher photon energies than the rest of the x-ray pulses. A multilayer x-ray mirror provided by the Center for X-Ray Optics was then used to filter out all of the lower energy pulses, leaving a single, isolated, attosecond duration soft x-ray pulse. This mirror also focused the attosecond x-ray pulse and the few-cycle laser pulse into the interaction region where they intersected an effusive gas jet target of atoms or molecules. By moving the inner portion of the mirror with respect to the outer portion (split-mirror configuration), a time delay could be introduced between the attosecond x-ray pulse and the few-cycle laser pulse, yielding temporal dynamics. Either photoelectrons or photoion-fragments released by the target were then detected by a time-of-flight electron/ion spectrometer or by a velocity map imagine apparatus; both instruments were homebuilt.

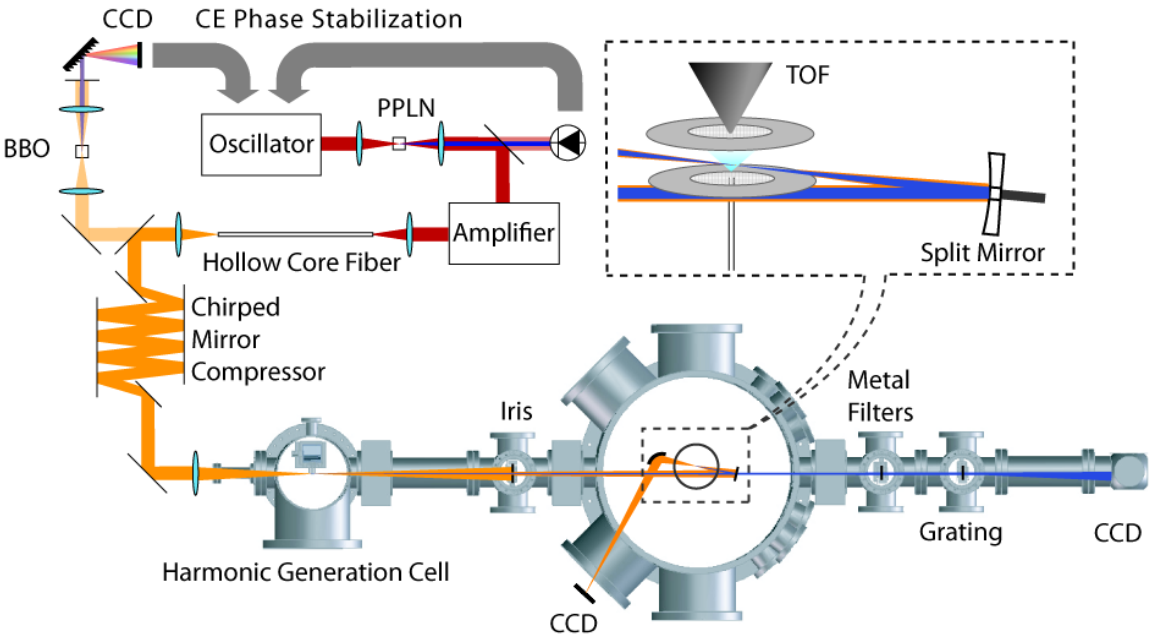

Figure 1. Experimental setup

The Leone/Neumark group was able to confirm isolated attosecond pulse production by experimentally mapping the vector potential of the driving laser pulse with sub-optical-cycle resolution in an atomic streaking experiment in Ne gas. Attosecond resolved measurements were also performed in gaseous SF_6 where streaked photoelectron spectra indicated that ionization from inner-valance molecular orbitals proceeded with no resolvable time delay compared to direct valence excitation.

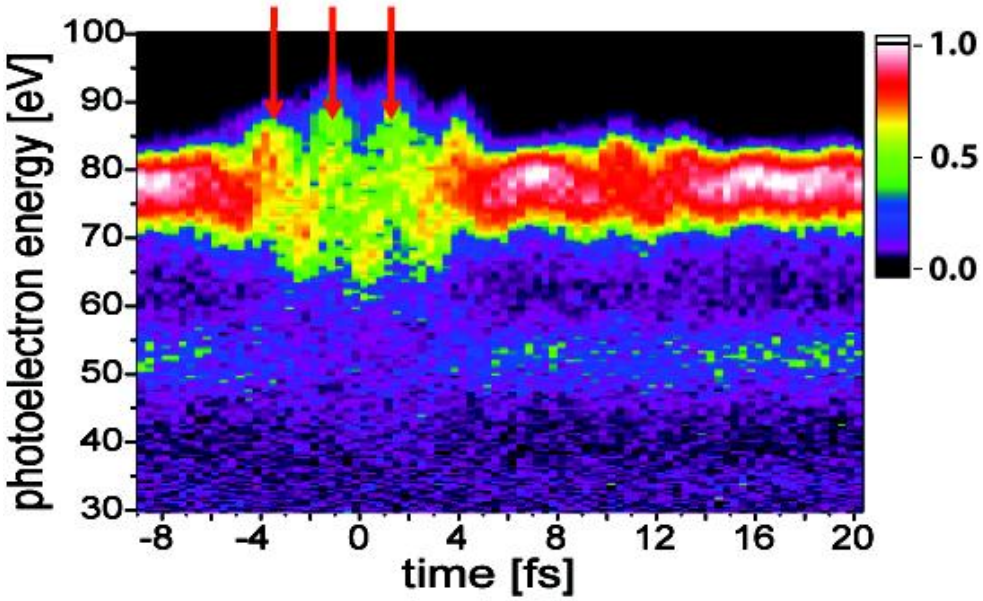

Figure 2. Photoelectron streak trace of the inner (53 eV) and outer (76 eV) valence electrons in SF_6. Red arrows show the sub-optical-cycle resolution indicative of an isolated attosecond pulse.

In addition to detection of emitted electrons, the Leone/Neumark group measured the photofragment yields of cations produced in the sub-femtosecond ionization of SF_6. In this case, dynamics were initiated with the attosecond XUV pulse and probed with the few-cycle laser pulse. Analysis of fragmentation patterns helped reveal which electronic potential surfaces were being accessed in the experiment, providing complementary information to photoelectron streaking studies.

As previously mentioned, another detector built in the Leone/Neumark group was a velocity map imaging (VMI) apparatus useful for determining both angular and kinetic energy distributions of photoelectrons. The VMI setup was used to measure CEP dependence in above threshold ionization in the perturbative, multiphoton ionization regime. Analysis found that the asymmetry of photoelectron angular distributions could be used to characterize the CEP and chirp of the laser pulse as well as the atomic phase of the transition.

The Leone/Neumark group also developed several new technical methods during the duration of the MURI grant. Among these were two new methods for producing isolated attosecond pulses: heterodyne gating and ionization gating. For the former, classical and quantum mechanical simulations of high harmonic generation driven by a two-color field showed that isolated attosecond pulses could be produced with much longer driving pulse lengths than previously demonstrated. In ionization gating, an ultrafast loss of phase matching was induced to limit the production of high harmonic radiation to only one or two optical half-cycles on the leading edge of the driving pulse. This method of generation relaxed the strict CEP and pulse duration requirements and allowed for tuning of the central frequency of the generated attosecond pulse. The isolated nature of the attosecond pulse was verified experimentally through a gas phase photoelectron streaking measurement. In another technical advancement, the Leone/Neumark group devised a method to quickly and easily measure and optimize the pulse-energy contrast between the main attosecond pulse and any satellite pulses *in situ*, important for maintaining the correct conditions for generating an isolated attosecond pulse in everyday operations.

III. EUV/Soft X-ray optics for femtosecond and attosecond source

Principal Investigator: David Attwood, Center for X-Ray Optics, LBNL, Berkeley

The Center for X-Ray Optics (CXRO) provided the MURI project with x-ray multilayer mirrors for various photon energies and supported the MURI project in a wide range of activities using its optics fabrication and calibration facilities. These activities included thin film sample preparation, filter calibration, gold coating of mirrors for infrared pulses, and surface scattering measurements.

The sputtering system in the CXRO multilayer lab coated multilayer mirrors used in the MURI project and was also used for other activities as mentioned above. The system consists of a three-target system with interchangeable targets to allow for sputtering of many different elements or compounds. It has accurate rate control of each layer thickness and a uniformity of 2.0% over a 4-inch surface. The CXRO calibration beamline (BL 6.3.2 at the Advanced Light Source) was used to characterize x-ray mirrors and filters used in the MURI project. The beamline gives accurate reflectivity and transmission measurements and has a high spectral resolution resolution of $\lambda/\Delta\lambda \sim 7000$. Along with high spectral purity and brightness, the beamline had a wide wavelength range of 25 nm to 1.0 nm (photon energies 50 – 1300 eV). During the period of MURI project, the CXRO team had extended the operation range to as low

as 25 eV, for better coverage of the photon energies used in various MURI experiments. The measurements performed at the beamline provided critical feedback to the mirror fabrication process, and ensured the quality of x-ray optics used in MURI experiments.

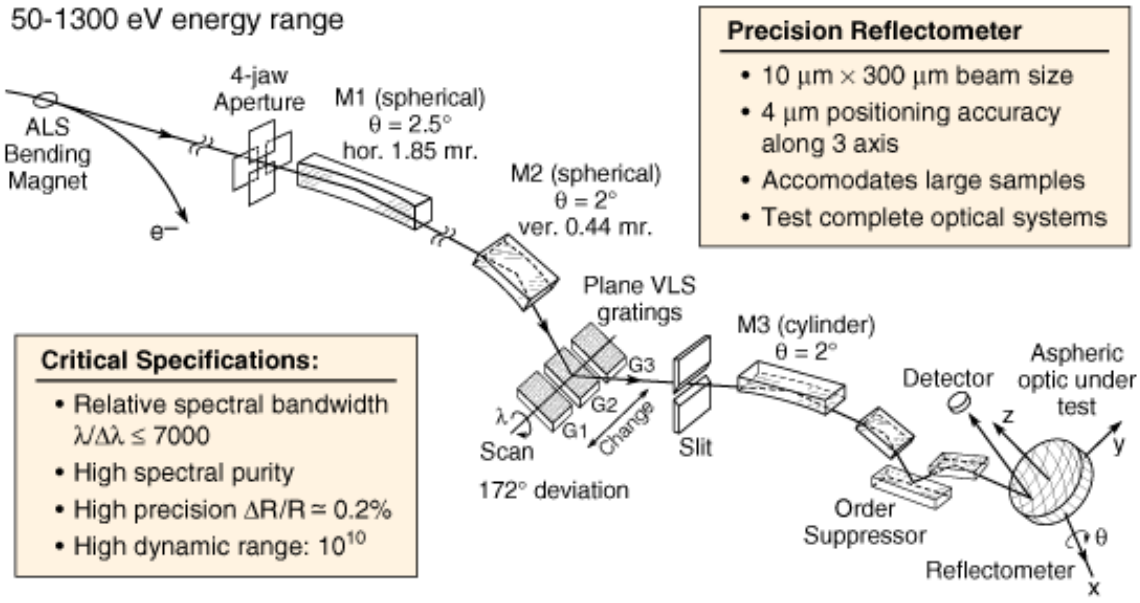

Fig. 1. CXRO calibration and characterization facility for EUV/soft x-ray optics transmission, reflection, and scattering measurements.

The central role of the CXRO team in the MURI project was to provide high efficiency multilayer mirrors for x-ray transportation, focusing, and spectral filtering. The CXRO team had extensive experience on Mo/Si multilayers, whose properties and fabrication procedures are well understood, and they work very well around wavelengths of 13 nm. For MURI experiments using photon energies near 90 eV, CXRO provided such mirrors with reflectivity approaching 70%. However, due to the increased absorption of both Mo and Si, at lower energies Mo/Si mirrors become much less efficient, for example the peak reflectivity will drop to less than 20% at 40 eV. To better support MURI experiments operating at lower energies, CXRO had developed Al- and Mg-based multilayer coatings that have much higher efficiencies at 30-70 eV range. Shown in fig. 2 are examples of those mirrors (together with a Mo/Si mirror at 90 eV).

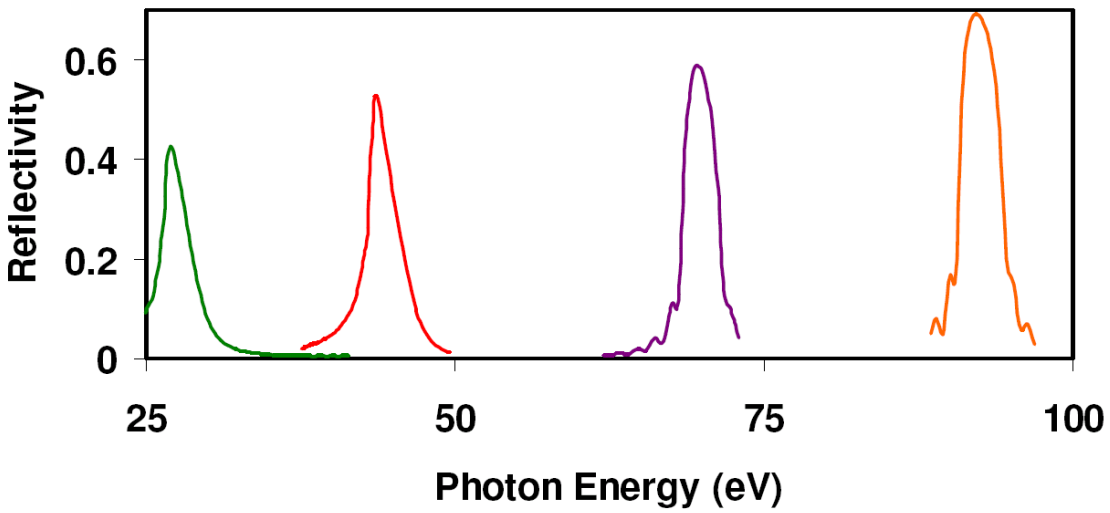

Fig.2. Measured reflectivity curves of various multilayers mirrors developed for MURI project.

Conventional multilayer structures are generally not optimized for high harmonic generation (HHG) source and ultrafast experiments, especially in attosecond regime. Multilayer coatings improve the total reflectivity through constructive interference between individual layers. This is a resonant process where only the wavelength satisfying a Bragg condition will be enhanced. Therefore, the increase of overall reflectivity inevitably results in a decrease of spectral bandwith the mirror can support. Since ultrafast pulses naturally have broad bandwidth, this put a serious constraint on the application of multilayer mirrors in attosecond experiments. For example, the widely used Mo/Si multilayer mirror with ~ 70% reflectivity only has a bandwidth of less than 4 eV. This effectively limits the shortest pulse duration to 450 attoseconds. To address this issue, the CXRO team investigated the possible variations of multilayer structures, and successfully fabricated a broadband mirror based on aperiodic multilayer structures with a flat reflectivity of near 20% across a bandwidth of 18 eV.

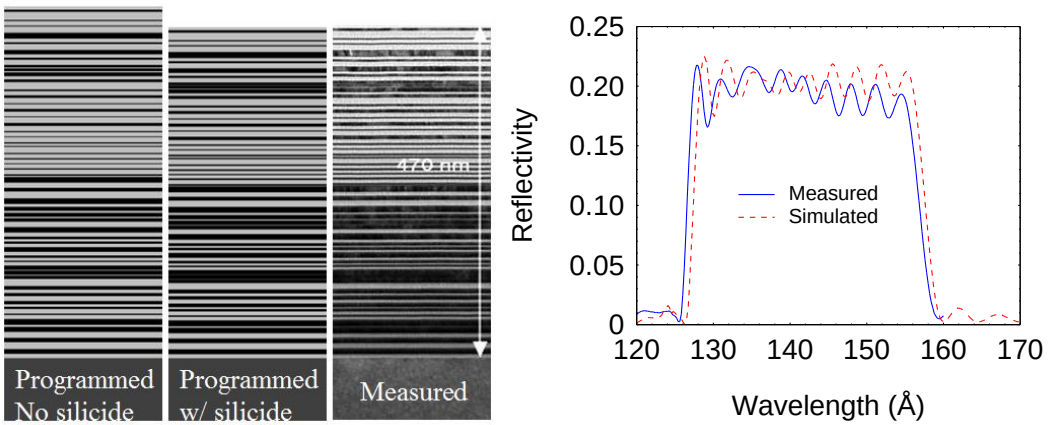

Fig.3 An aperiodic multilayer mirror coated at CXRO with ~ 18 eV bandwidth, wide enough to support ~ 100 attosecond pulse.

Besides broader bandwidth, aperiodic multilayer structures also hold the promise of altering the spectral phase of ultrafast pulses, thus providing a mechanism for pulse shaping in the attosecond

regime. Theoretical models and experiment results have shown the existence of an intrinsic chirp from the HHG process; i.e. different photon energies are emitted at different times. A 'chirped' multilayer mirror with adequate phase response can be used as a pulse compressor to compensate the intrinsic chirp and fully take advantage of the ultrabroad bandwidth coherent radiation of the HHG source, thus providing the shortest pulse possible. It is critical to accurately measure the phase response of an aperiodic structure, as small deviation of layer thickness in an aperiodic structure would change the phase response dramatically. The CXRO team had demonstrated an effective method using total electron yield from multilayer surfaces to measure the phase response of chirped multilayers, eliminating the requirement of precise positioning in typical interferometic measurements.

IV. Nanostructure design/optical and mechanical perturbations

Principal Investigator: A. Paul Alivisatos, University of California, Berkeley

The Alivisatos group completed multiple studies of semiconductor nanocrystals under the influence of strong optical and mechanical perturbations.

At high ultraviolet excitation fluences, laser-induced melting of rod-shaped CdSe nanocrystals was observed (Figure 1). An attempt to time resolve the melting dynamics of CdSe and CdTe nanocrystals, using second harmonic scattering as a probe of the centrosymmetry loss upon melting, led to the discovery of enhanced second harmonic scattering from photoexcited nanocrystals. Saturation in the relative enhancement per excited electron indicated the presence of a dense electron-hole plasma in the nanocrystals, which exhibited a more harmonic response to the laser field with increasing carrier density (Fig. 2).

The rapid excitation of a high density of electron-hole pairs also resulted in the generation of coherent acoustic phonons in CdSe spherical and rod-shaped nanocrystals. The phonon frequencies were not dependent upon the incident laser fluence, indicating the stability of the nanocrystal elastic constants during intense excitation. The phonon modes created were determined to be radial, not longitudinal, based on the lack of rod length dependence of the phonon frequency, while a frequency dependence on particle radius was observed (Fig. 3).

The wurtzite to rocksalt polymorphic phase transformation in CdSe nanocrystals was studied using laser-induced shock waves (Fig. 4). Under shock compression, the nanocrystals transformed under the influence of an applied pressure of 3.2 GPa, a significantly lower pressure than the 7GPa required to transform nanocrystals under hydrostatic compression in a diamond anvil cell (Fig. 5). This was attributed to the shear stress resulting from uniaxial shock compression. Additionally, the transformation was complete within 100 ps, exhibiting significantly faster kinetics than observed under hydrostatic compression. This approached the timescale for individual particle transformation, determined from recent simulations to be 7-50 ps. The kinetics became faster with increasing shock pressure, indicating a faster nucleation rate with higher instantaneous stress (Fig. 6). At the highest shock pressure studied, 3.75 GPa, the particularly rapid nucleation rate may indicate that each particle undergoes multiple nucleation events.

Laser-induced shock waves were also used to induce the fracture of hollow CdS nanospheres (Fig. 7). Hollow nanospheres exhibited a greater degree of fragmentation when subjected to a higher applied shock stress (Fig. 8). A time resolved experiment was performed to measure the attenuation of an incident shock wave by a layer of hollow particles, which was determined to be 0.5GPa for a 2.5GPa shock (Fig. 9). This was consistent with the fracture stress determined by a previous single-particle hollow sphere compression experiment.

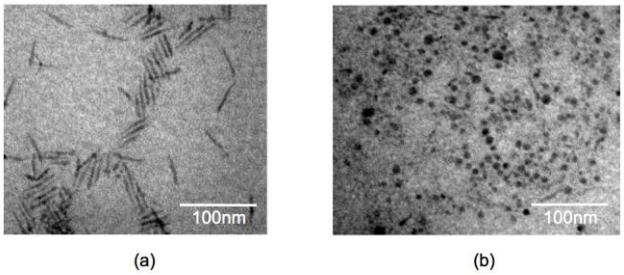

Figure 1: (a) 40 nm x 5 nm CdSe nanorods. (b) Same nanorod sample after irradiation by a 35 μJ laser pulse.

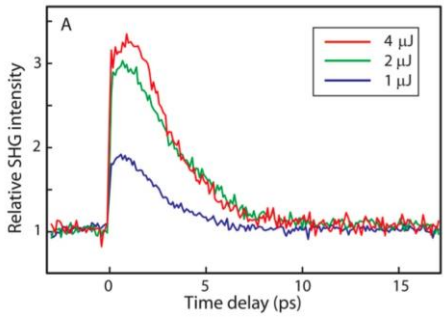

Figure 2: Time resolved second harmonic generation from CdTe nanocrystals.

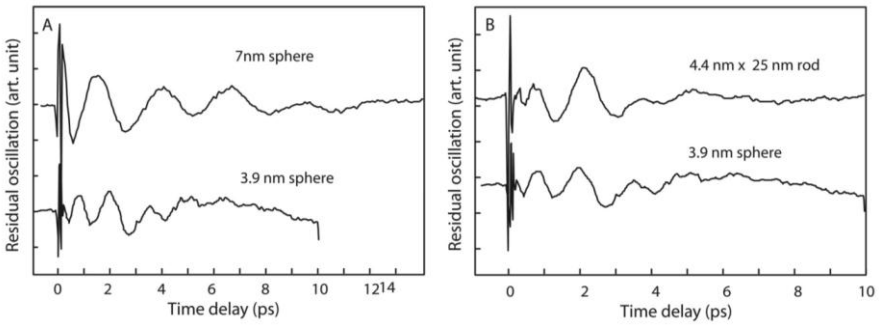

Figure 3: Coherent acoustic phonon oscillations in CdSe (a) nanospheres. (b) Sphere-rod comparison.

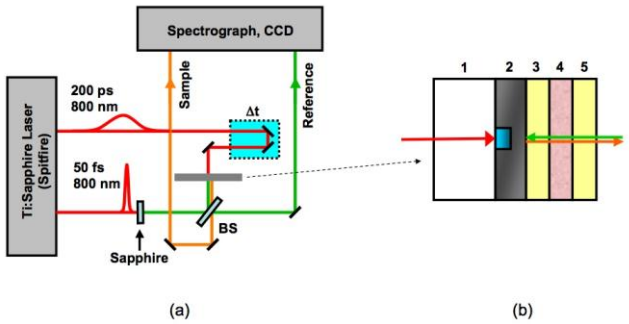

Figure 4: Schematic of (a) experimental apparatus and (b) shock target consisting of 1: glass, 2: aluminum, 3: polymer buffer layer, 4: polymer layer containing CdSe nanocrystals, 5: polymer overlayer.

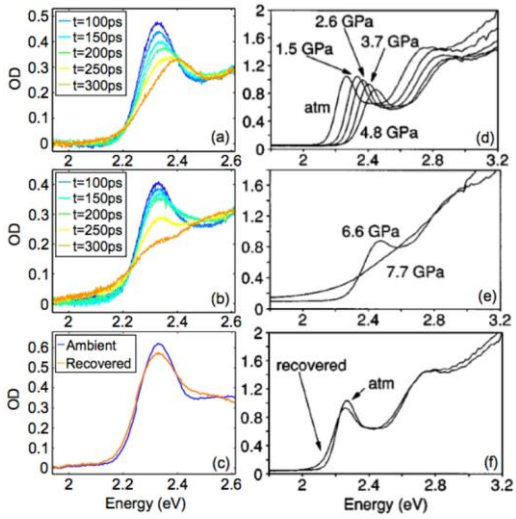

Figure 5: Absorption spectra of CdSe nanocrystals under (a) 2.3 GPa shock and (b) 3.2 GPa shock. (c) Spectrum many minutes after experiment. (d),(e),(f) are the corresponding spectra of CdSe nanocrystals under hydrostatic compression, from previous work published by the Alivisatos group.

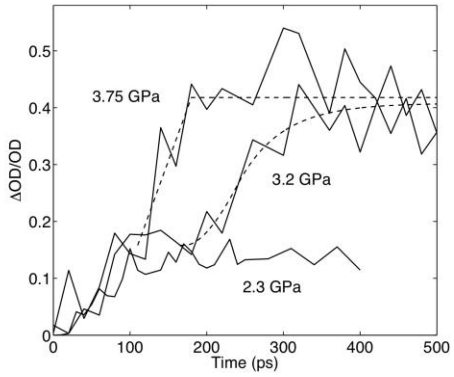

Figure 6: Disappearance of wurtzite CdSe nanocrystal excitonic feature following shock compression to various peak stresses.

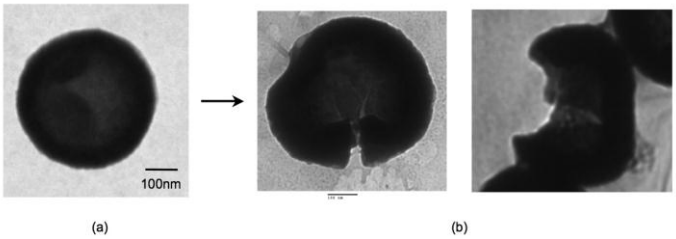

Figure 7: Shock-induced fracture in CdS hollow nanospheres.

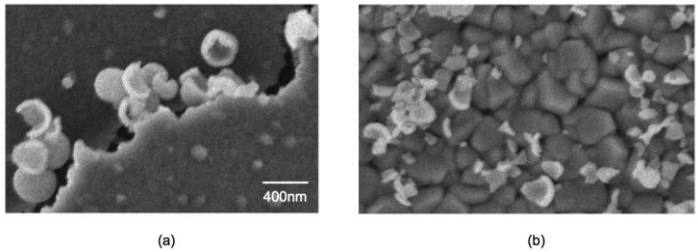

Figure 8: Hollow nanospheres following shocks induced by (a) 120 μJ laser pulse (b) 160 μJ laser pulse.

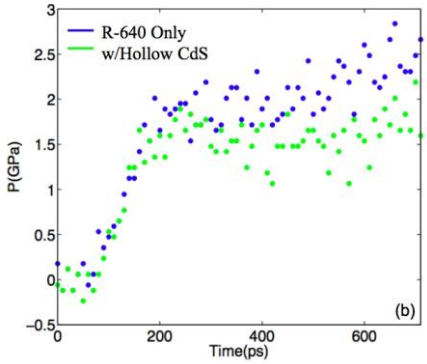

Figure 9: Response of R-640 pressure sensitive dye to a shock that has traversed a polymer layer containing hollow nanospheres, compared with the R-640 response when no hollow nanospheres are present in the polymer layer.

V. Laboratory for XUV Attosecond Studies of Electron Dynamics in Solids

Principal Investigators: Robert Kaindl (Chemla group), Robert Schoenlein (Shank group), LBNL and University of California, Berkeley

The aim of the condensed-matter attosecond effort was to develop a dedicated instrument to carry out studies of electron dynamics in solids on their natural attosecond temporal and eV energy scales. The periodic lattice of a solid leads to fundamentally new physics of electron dynamics as compared to atomic and molecular systems, including the interplay of itineracy and localization in correlated electron systems, quantum kinetics of many-particle interactions, plasmonic dynamics of confined electrons, or coherent quantum mechanical oscillations of charges accelerated in high electric fields.

Since solid state experiments necessitate quite different conditions compared to gas phase studies, a dedicated laboratory for condensed matter attosecond science was constructed by Kaindl, Schoenlein, and colleagues. It provides the necessary parameters, e.g. variable excitation density, tunable streak wavelengths, reconfigurable beam geometry, and suitable vacuum conditions. Part of the setup is shown in Fig. 1(a). At the outset, an existing 1-kHz Ti:sapphire amplifier system (Femtolasers Inc.) with grating-less design was used to produce 800 uJ, 28-fs duration pulses at 800-nm wavelength. To generate few cycle pulses, a gas-filled hollow-core fiber with 250 μm diameter was used, into which the amplifier pulses are focused. Optimal conditions were obtained with Ne gas at ~10 psi pressure, yielding broad spectra that span ~600-900 nm. The fiber output was recompressed with a chirped mirror compressor while tuning the dispersion with thin glass wedges, yielding extremely short optical pulses of merely 6.5-fs duration (full width at half maximum, FWHM) as verified with a self-constructed autocorrelator.

Attosecond pulse production necessitates the stabilization of the carrier envelope phase of the sub-7 fs pulses. To this end, a highly compact f-2f interferometer was first constructed to stabilize the oscillator seed pulses. For maximum stability, the f-2f interferometer was tailored to fit inside the small available 25 cm x 25 cm space within the Ti:sapphire amplifier enclosure. Whitelight generation proceeds within a 40-mm long photonic crystal fiber, with sealed ends ensuring long-term stability. The complex phase locking electronics for this interferometer was supplied by Jun Ye's group within the MURI collaboration. The oscillator was successfully stabilized with this "fast loop" interferometric setup after observation of the carrier-envelope beat signal. In turn, the amplifier output was stabilized with a second, external "slow loop" f-2f setup, with feedback control based on spectral fringe pattern analysis using a computer-controlled fiber spectrometer. Overall, this setup allows, meanwhile, routine stabilization of the carrier envelope phase of the amplified pulses for attosecond pulse production.

An important aspect of the condensed matter capability developed in this MURI was the realization that tunable few-cycle mid-infrared (mid-IR) streak fields are of key importance to solid-state attosecond streaking studies. First, the threshold for damage is much lower than in gas phase systems, such that longer wavelengths are necessary to undercut the two-photon absorption threshold due to bandgap excitations. Second, the electron ponderomotive potential

scales with the square of the wavelength, so that much lower field strengths (and, hence, laser intensities) can be used in the mid-IR to achieve the same energy shift. Third, tunable streak fields allow for optimal tailoring of the streaking time window to the solid state electron dynamics. Finally, tunable coherent few-cycle mid-IR pulses allow resonant excitation of low-energy degrees of freedom and charge acceleration to study electron behavior in high electric fields.

Thus, the condensed matter atto lab was equipped with synchronized soures of mid-IR pulses. A new scheme was demonstrated for generation of phase-stable broadband mid-IR pulses directly from the 6.5 fs pulses out of the hollow core fiber compressor. Few-cycle mid-IR pulses are often generated by intricate cascades of optical parametric amplification and difference frequency mixing. In such schemes, however, the carrier-envelope phase is not automatically stable. In contrast, a significantly more compact route involves mixing components within the broad spectrum of individual, visible fs pulses, which entails intrinsic CE phase stability. This scheme was demonstrated earlier by Kaindl et al. in GaSe, but limited to frequencies below 50 THz. In the MURI project, the Kaindl group successfully demonstrated generation of mid-IR pulses using phase-matched difference frequency mixing in $LiIO_3$. For this, a train of 6.5-fs, 200 μJ pulses from the hollow core fiber compressor was transmitted unfocussed through a 113-μm thick $LiIO_3$ crystal. Type-I phase matching resulted in generation of extremely broadband, octave spanning mid-IR pulses covering 50-130 THz. Theory calculations yielded excellent agreement with experiment. The measured pulse energy of ~8 nJ corresponds to 5 MV/cm field strength when focused to a 50 μm spot. This equals the ponderomotive potential previously used for attosecond streaking with near-IR pulses, but is achieved at much lower field strength and longer wavelengths (~3-4 μm), i.e. optimal conditions for solid state streaking.

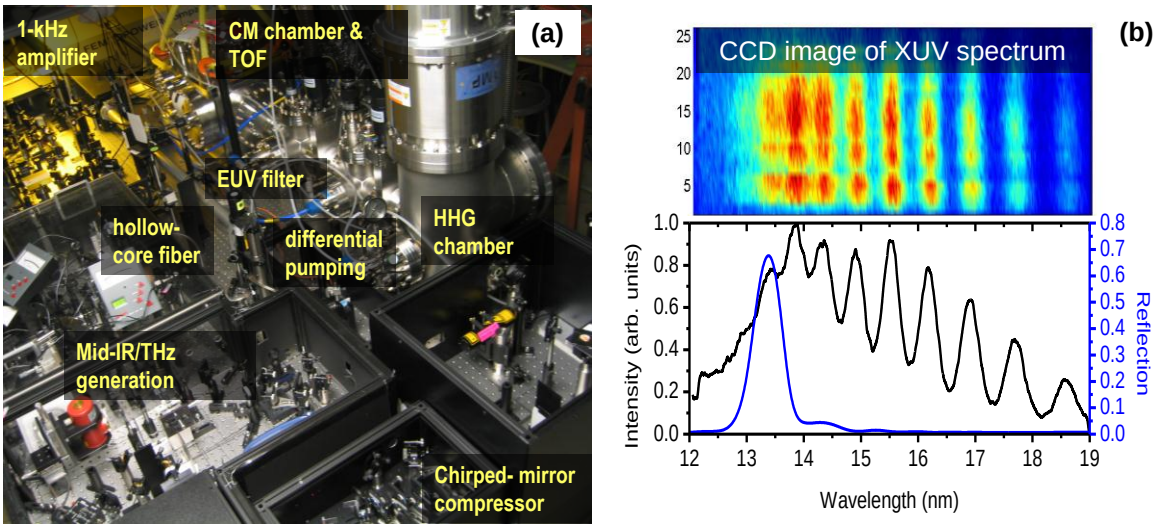

Fig. 1 (a) Attosecond condensed-matter lab. (b) CCD image and spectrum of XUV high-harmonic pulses generated in Ne gas (black line), and reflectivity of MoSi mirror (blue).

The next step of the project encompassed the production of XUV pulses via high-harmonic generation (HHG) in a chamber whose design followed the gas phase setup. Pulses with up to ≈100 eV photon energy were obtained by focussing carrier envelope phase-stabilized 6.5-fs pulses from a 1-kHz amplifier into Ne gas. This resulted in a laser-like XUV beam (≈10^{10} - 10^{11} photons/s) with low divergence, which was then steered along with the near-IR pulse into a unique experiment chamber optimized for the condensed matter experiments (see below). The XUV harmonic spectrum was assessed with a spectrometer consisting of a XUV transmission grating and XUV CCD camera. A typical measured CCD image and corresponding spectrum is shown in Fig. 1(b). The XUV pulses were optimized in the region around 95 eV to coincide with the high reflectivity region of the multi-layer MoSi mirror used for focusing of the XUV pulses in the experiment chamber.

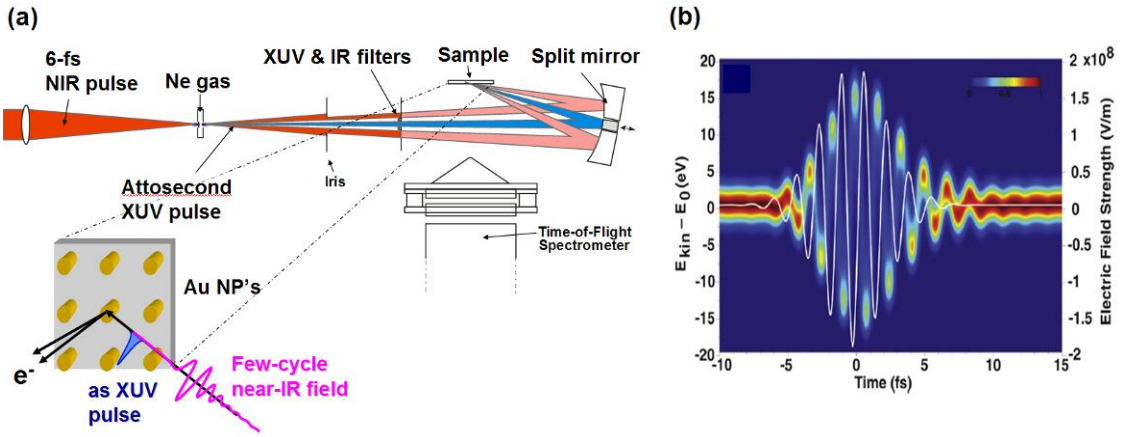

Fig. 2 (a) Plasmon sample and experimental setup, (b) plasmon dynamics simulation.

Plans for several initial attosecond condensed matter experiments with this setup were developed by the MURI collaboration. As a first key experiment, the Leone group developed a scheme for studying coherent particle-plasmon dynamics in Au nanoparticles. In these experiments, the near-IR laser pulse is used to coherently drive the collective oscillations of electrons. A time-delayed attosecond XUV pulse photoemits conduction band electrons which are ponderomotively accelerated or decelerated by the plasmon field. The strong plasmon field will lead to large delay-time dependent shifts (on the order of 10's eV) in the photoelectron spectra that directly reflect the plasmon near-field dynamics and, in turn, the nanoscale coherent electron motion. The setup is illustrated in Fig. 2(a). This conceptually new scheme can extract plasmon dynamics directly from time-dependent photoelectron spectra. Simulations of the attosecond dynamics and preliminary experiments using near-IR laser pulses and multiphoton ionization in Au nanoparticles were carried out by the Leone and Neumark groups. These studies provided a gauge of the plasmon-field ponderomotive forces. Attosecond experiments were prepared by developing the condensed matter setup and suitable samples. The decay of the coherent plasmon polarization will be directly evident in the time-resolved photoelectron spectra, as shown in the simulation in Fig. 2(b).

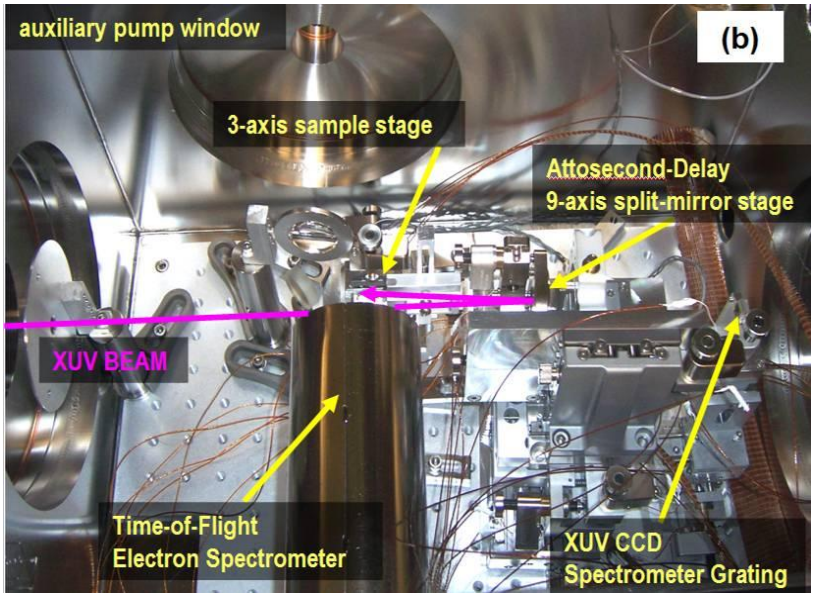

Fig. 3 Components inside vacuum chamber optimized for attosecond experiments on solid-state materials.

For these and other experiments, an experiment chamber uniquely optimized for condensed matter studies was designed, assembled, and integrated into the condensed matter attosecond XUV beamline by Kaindl and coworkers. The internal components are shown in Fig. 3. A piezo-controlled split mirror separately reflects XUV and near-IR pulses for precise timing delay. The MoSi mirror reflectivity cuts out a ~4-eV bandwidth from the harmonics allowing for > 500 *as* duration. Emitted photoelectrons from the sample are detected with a time-of-flight (TOF) spectrometer (important photoemission space charge limitations were also explored in collaboration with the Lanzara group). Differential pumping between the generation and experiment chamber was employed to reduce the vacuum level. A breadboard allows for reconfiguration into different experimental configurations (transmission, TOF, etc). An important aspect for solid state attosecond studies was the concurrent availability of tunable mid-IR pulses mentioned above, which can be coupled in through an auxiliary window. At present, all internal components of the vacuum beamline were fully completed and functional. This includes motorized multi-axis UHV-compatible mounts, enabling the delivery of both pump and probe pulses onto target. Specifically, a ten-axis stage provides for focusing, alignment and delay of the pulses. A TOF electron spectrometer was commissioned for the execution of time-resolved photoemission measurements in condensed matter targets. Adjustable apertures and pellicle XUV/near-IR filters allow control of the strong pump attenuation necessary for solid state experiments.

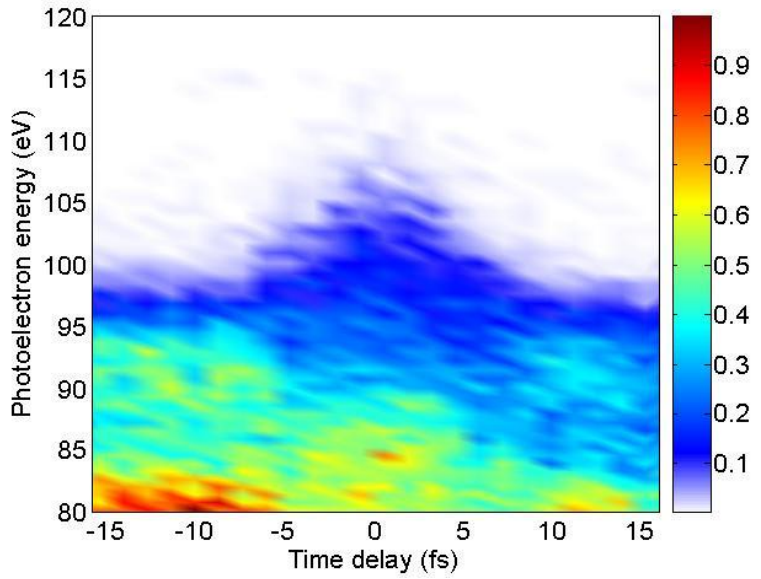

Fig. 4. Demonstration of time-resolved streaking of photoelectrons emitted from a solid-state ITO target with 90-eV XUV pulses, using 6.5 fs near-IR pulses for ponderomotive acceleration. The energy shift of around 10 eV exceeds the XUV pulse bandwidth.

With this setup, the Kaindl and Leone groups have performed recent measurements demonstrating near-IR streaking of photoelectrons generated by the XUV pulse in a solid sample. This demonstration is an important step towards the realization of the attosecond plasmon studies. A first such result is shown in Fig. 4. An optimized array of 300-nm high Au nanopillars was also designed for fabrication at the Molecular Foundry. A 3:1 aspect ratio ensures a plasmon peak resonant to the driving field spectrum centered around ~750 nm. The Au nanoparticle geometry was tailored for maximizing the ponderomotive potential due to a surface-normal dipole that points towards the TOF spectrometer. Thus, the setup in the condensed matter laboratory has been completed and photoelectron experiments utilizing few-cycle near-IR streak fields combined with 95 eV XUV pulses are underway. Results on the plasmon dynamics are imminent. Further plans for ground-breaking attosecond condensed matter science were developed by Kaindl to study electronic coherence, fundamental limitations of electron acceleration, quantum kinetics and energy relaxation in graphene and other nanosystems, and the transient band structure of correlated-electron materials. All these studies can take advantage of the world-unique condensed matter attosecond instrumentation developed as part of this MURI effort.

Cumulative Publications

R. J. Jones and J. Ye, "High-repetition rate, coherent femtosecond pulse amplification with an external passive optical cavity," Opt. Lett. 29, 2812 (2004).

R.J. Jones, K.D. Moll, M.J. Thorpe, and J. Ye, "Phase-coherent frequency combs in the vacuum ultraviolet via high-harmonic generation inside a femtosecond enhancement cavity," Phys. Rev. Lett. 94, 193201 (2005).

M. J. Thorpe, R. J. Jones, K. D. Moll, J. Ye, and R. Lalezari, "Precise measurements of optical cavity dispersion and mirror coating properties via femtosecond combs," Opt. Express 13, 882 (2005).

K. D. Moll, R. J. Jones, and J. Ye, "Nonlinear dynamics inside femtosecond enhancement cavities," Opt. Express 13, 1672 (2005).

M. J. Thorpe, K. D. Moll, R. J. Jones, B. Safdi, and J. Ye, "Broadband cavity ringdown spectroscopy for sensitive and rapid molecular detection," Science 311, 1595 (2006).

K. D. Moll, R. J. Jones, and J. Ye, "Output coupling methods for cavity-based high-harmonic generation," Opt. Express 14, 8189 (2006).

M. J. Thorpe, D. D. Hudson, K. D. Moll, K. Lasri, and J. Ye, Opt. Lett. 32, 307 (2007).

I. Hartl, T. R. Schibli, A. Marcinkevicius, M. E. Fermann, D. C. Yost, D. D. Hudson, and J. Ye, "Cavity-enhanced similariton Yb-fiber laser frequency comb: 3 x 10^{14} W/cm^2 peak intensity at 136 MHz," Opt. Lett. 32, 2870 (2007).

E. E. Eyler, D. E. Chieda, M. C. Stowe, M. J. Thorpe, T. R. Schibli, and J. Ye, "Prospects for precision measurements of atomic helium using direct frequency comb spectroscopy," Eur. Phys. J. D 48, 43 – 55 (2008).

M. J. Thorpe, D. Balslev-Clausen, M. Kirchner, and J. Ye, "Human breath analysis via cavity-enhanced optical frequency comb spectroscopy," Opt. Express 16, 2387 – 2397 (2008).

D. C. Yost, T. R. Schibli, and J. Ye, "Novel geometry for output coupling of intracavity high harmonic generations," Opt. Lett. 33, 1099 – 1101 (2008).

T. R. Schibli, I. Hartl, D. C. Yost, M. J. Martin, A. Marcinkevičius, M. E. Fermann, and J. Ye, "Optical frequency comb with sub-mHz linewidth and >10 W average power," Nature Photonics 2, 355 – 359 (2008).

M. J. Thorpe and J. Ye, "Cavity-enhanced direct frequency comb spectroscopy," Appl. Phys. B 91, 397 – 414 (2008).

M. J. Thorpe, F. Adler, K. C. Cossel, M. H. G. de Miranda, and J. Ye, "Tomography of a supersonically cooled molecular jet using cavity-enhanced direct frequency comb spectroscopy," Chem. Phys. Lett. 468, 1 – 8 (2009).

D. C. Yost, T. R. Schibli, J. Ye, J. L. Tate, J. Hostetter, K. J. Schafer, M. B. Gaarde, "Below-threshold harmonics for VUV frequency combs," Phys. Rev. Lett., submitted (2009).

"Single attosecond pulse generation in the multicycle-driver regime by adding a weak second-harmonic field", T. Pfeifer, L. Gallmann, M.J. Abel, D.M. Neumark, and S.R. Leone, Opt. Lett. **31**, 975-977 (2006).

"Circular phase mask for control and stabilization of single optical filaments", Thomas Pfeifer, Lukas Gallmann, M.J. Abel, D.M. Neumark, and S.R. Leone, Opt. Lett. **31**, 2326-2328 (2006).

"Heterodyne mixing of laser fields for temporal gating of high-order harmonic generation", T. Pfeifer, L. Gallmann, M.J. Abel, P.M. Nagel, D.M. Neumark, and S.R. Leone, Phys. Rev. Lett. **97**, 163901 (2006).

"Comparison of the filamentation and the hollow-core fiber characteristics for pulse compression into the few-cycle regime", L. Gallmann, T. Pfeifer, P.M. Nagel, M.J. Abel, D.M. Neumark, and S.R. Leone, Appl. Phys. B – Lasers and Optics **86**, 561-566 (2007).

"Isolated attosecond pulses using a detuned second-harnomic field", H. Merdji, T. Auguste, W. Boutu, J. Pascal Caumes, B. Carré, T. Pfeifer, A. Jullien, D.M. Neumark, and S.R. Leone, Opt. Lett. **32**, 3134-3136 (2007).

"Generating coherent broadband continuum soft-x-ray radiation by attosecond ionization gating", T. Pfeifer, A. Jullien, M.J. Abel, P.M. Nagel, L. Gallmann, D.M. Neumark, and S.R. Leone, Opt. Exp. **15**, 17120-17128 (2007).

"Time-resolved spectroscopy of attosecond quantum dynamics", T. Pfeifer, M.J. Abel, P.M. Nagel, A. Jullien, Z-H. Loh, M.J. Bell, D.M. Neumark, and S.R. Leone, Chem. Phys. Lett. **463**, 11-24 (2008). (Frontiers Article)

"Ionization phase-match gating for wavelength-tunable isolate attosecond pulse generation", A. Jullien, T. Pfeifer, M.J. Abel, P.M. Nagel, M.J. Bell, D.M. Neumark, and S.R. Leone, Appl. Phys. B – Lasers and Optics **93**, 433-442 (2008).

"Carrier-envelope phase-dependent quantum interferences in multiphoton ionization", M.J. Abel, T. Pfeifer, A. Jullien, P.M. Nagel, M.J. Bell, D.M. Neumark, and S.R. Leone, J. Phys. B: At. Molec. Opt. Phys. **42**, 075601 (2009).

"Measurement and optimization of isolated attosecond pulse contrast", T. Pfeifer, M.J. Abel, P.M. Nagel, W. Boutu, M.J. Bell, Y. Liu, D.M. Neumark, S.R. Leone, Opt. Lett., In Press (2009).

A. L. Aquila, F. Salmassi, F. Dollar, Y. Liu and E. Gullikson, "Developments in Realistic Design for Aperiodic Mo/Si Multilayer Mirrors", Opt. Exp. **14** (21), 10073-10078 (2006).

Andrew Aquila, Farhad Salmassi, and Eric Gullikson, "Metrologies for the phase characterization of attosecond extreme ultraviolet optics," Opt. Lett. **33**, 455-457 (2008).

D. H. Son, J. S. Wittenberg, U. Banin and A. P. Alivisatos, "Second Harmonic Generation and Confined Acoustic Phonons in Highly Excited Semiconductor Nanocrystals," J. Phys. Chem. B, **110**(40): 19884-19890 (October 2006)

Joshua Saul Wittenberg, "The Behavior of Semiconductor Nanocrystals Under Intense Ultraviolet Irradiation and Shock Wave Compression," UC Berkeley Department of Chemistry Doctoral Thesis, (December, 2008).

Joshua Wittenberg, Maxwell G. Merkle, A. Paul Alivisatos; "Wurtzite to Rocksalt Structural Phase Transformation in CdSe Nanocrystals by Laser-Induced Shock Waves." (To Be Submitted)

T. Zentgraf, R. Huber, N. C. Nielsen, D. S. Chemla, R. A. Kaindl, "Ultrabroadband 50-130 THz pulses generated via phase-matched difference frequency mixing in LiIO3" Opt Exp. **15**, 5775 (2007).

J. Graf, C. Jozwiak, C. Smallwood, R. A. Kaindl, and A. Lanzara, "Vacuum space charge effects in laser-based solid-state photoemission spectroscopy", under submission to J. Appl. Phys (2009).

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